

SELECTIVE GENERATION OF FERRAENOLATES, $\text{Li}[\text{CpFe}(\text{CO})_2\text{COCR}^1\text{R}^2]$, AND THEIR REACTIONS WITH ELECTROPHILES

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Summary

The acyliron complex, $\text{CpFe}(\text{CO})_2\text{COCHR}^1\text{R}^2$, is converted to the corresponding ferraenolate, $\text{Li}[\text{CpFe}(\text{CO})_2\text{COCR}^1\text{R}^2]$, by the action of $\text{LiN}(\text{SiMe}_3)_2$ at low temperature. The resulting ferraenolate reacts with electrophiles and, in some cases, reversible elimination of the ketene fragment ($\text{R}^1\text{R}^2\text{C}=\text{C}=\text{O}$) is observed.

Introduction

Metallaenolates, $[\text{M}-\text{COCH}_2]^-$ [1], have recently attracted much attention not only as a methylenecarbonyl ($\text{CO}-\text{CH}_2$) dianion equivalent [1a–d] but also as a synthon for binuclear μ -ketene complexes, $\text{MCOCH}_2\text{M}'$ [1g], which are recognized as a key intermediate in the homologation step of the Fischer–Tropsch synthesis [2].

In order to accomplish selective synthesis by means of metallaenolates, which are usually generated by deprotonation of acylmetal complexes, it is essential to clarify the factors controlling the reactivity of the acyliron complexes toward strong bases and the stability of the resulting enolates.

In this article we describe the selective generation of ferraenolates, $\text{Li}[\text{CpFe}(\text{CO})_2\text{COCR}^1\text{R}^2]$, from acyliron complexes, $\text{CpFe}(\text{CO})_2\text{COCHR}^1\text{R}^2$, possessing two feasible acidic reaction sites (the acyl proton α to the carbonyl group and protons on the cyclopentadienyl ring) and some reactions with electrophiles are also disclosed. Although there have been several reports on generation of ferraenolates from phosphine-substituted acyl complexes, $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COCHR}^1\text{R}^2$ [1a–d], some different aspects are revealed by our study. Very recently, Helquist et al. have independently achieved the generation of the same ferraenolate and described some reactions in a communication [1e].

Results and discussion

Generation of ferraenolate

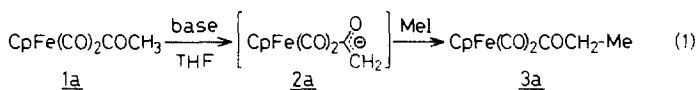
Initially we attempted generation of the ferraenolate (**2a**) from acetylcyclopenta-

TABLE I
PROTON ABSTRACTION FROM ACYLIRON COMPLEXES I

base	LiN(SiMe ₃) ₂	LiNPr ₂ ⁱ (LDA)
CpFe(CO) ₂ COCHR ₁ R ₂ (1)	Product ratio, 3 : 4 ^a (Total yield, %)	
1a (R ₁ = R ₂ = H)	100 : 0 (90) ^b	72 : 28 (95) ^a
1b (R ₁ = H, R ₂ = Me)	100 : 0 (77) ^b	0 : 100 (92) ^{a,c}
1c (R ₁ = R ₂ = Me)	no reaction	0 : 100 (96) ^b

a: determined by ¹H NMR, b: isolated yield, c: **4c** was also formed (See text).

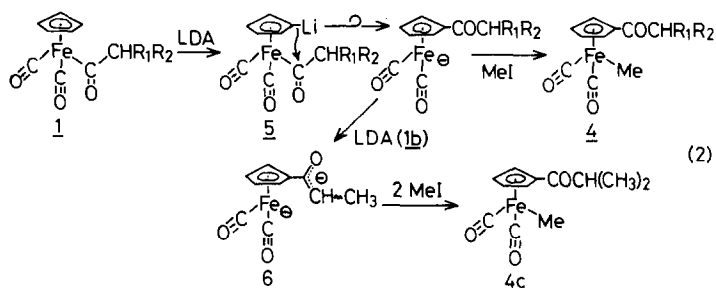
dienyldicarbonyliron (**1a**) by the action of a strong base in THF at low temperature and the reaction was monitored by quenching the anionic species with MeI (eq. 1). Among the bases employed, NaH, n-BuLi, LDA* and LiN(SiMe₃)₂, the latter two



gave the expected propionyl complex **3a** in 68 and 90% yields, respectively, although NaH left **1a** unaffected and n-BuLi gave an unidentified green paramagnetic complex. Furthermore, the rearranged methyl complex **4a** was also produced in the case of LDA (vide infra).

Homologues of acyl complexes **1b** and **1c** were similarly treated with LDA or LiN(SiMe₃)₂, followed by quenching with MeI and the results are summarized in Table I. (Results for **1a** are reproduced.) The enolate adducts **3a** and **3b** were formed with 100% selectivity by the use of LiN(SiMe₃)₂ and, in marked contrast to these results, LDA predominantly afforded the methyl complexes **4a-c**. The structure of **4** was confirmed by the ¹H NMR signals appearing at δ 4.9 (2H) and 5.3 (2H) ppm. They respectively exhibited a triplet-like coupling pattern which was characteristic of the monosubstituted cyclopentadienyl group [3]. The singlet signal (3H) at higher field designated the presence of a methyl group directly bound to the iron nucleus. The methyl complexes **4** originated from the initial lithiation at the cyclopentadienyl ring and subsequent acyl group migration [4] followed by methylation at the iron nucleus (eq. 2).

* Abbreviations: LDA = lithium diisopropylamide (LiNPr₂). Cp = η⁵-cyclopentadienyl.



In the case of the propionyl complex **1b** an excess of LDA generated dianion **6**, which gave **4c** upon methylation. Thus, the product ratio **3/4** should correspond to the ratio of the initially generated anionic species, **2/5**. In conclusion, $\text{LiN}(\text{SiMe}_3)_2$ selectively abstracted the acyl proton α to the carbonyl group and LDA predominantly attacked the cyclopentadienyl ring.

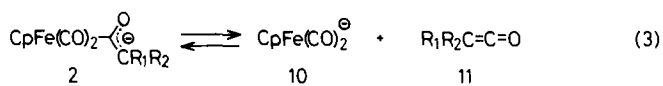
These results should be viewed in the light of the steric interaction between the acyl complex and the base. The less bulky base, LDA, tends to abstract a more acidic proton attached to the cyclopentadienyl ring. On the other hand, the more bulky $\text{LiN}(\text{SiMe}_3)_2$ is virtually inaccessible to the sterically congested cyclopentadienyl proton so that the less congested acyl proton is detached. To date most examples of metallaenolates [1], with only one exception [4b], showed lithiation at the cyclopentadienyl ring to be prevented either by the introduction of bulky ligands such as a tertiary phosphine or by the use of a bulky base.

In accord with this steric consideration $\text{LiN}(\text{SiMe}_3)_2$ could not abstract any proton from isobutyryl complex **1c** and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COCH}_3$, while the latter complex was readily converted to the enolate by LDA as reported by Davies and Liebeskind [1a-d].

Reactions of ferrocenolate **2** with electrophiles and elimination of ketene fragment

The resulting ferrocenolate **2a** was successively treated with various electrophiles such as alkyl halides, carbonyl compounds and metal halides at low temperature.

Among the alkyl halides employed only MeI gave the enolate adduct **7** and others gave the corresponding alkyl complexes **8** accompanied by a decomposition product, $[\text{CpFe}(\text{CO})_2]_2$ (**9**) [5] (Table 2). Furthermore, when the ferrocenolate **2a** was treated with MeI at room temperature, the adduct **3a** was not obtained at all and the methyl complex **4a** was obtained in 13% yield together with **9** (27%). These results suggested that the ferrocenolate **2** was in equilibrium with the parent ferrate **10** and ketene **11** at higher temperature ($> -50^\circ\text{C}$) (eq. 3). In fact the liberated ketene **11a**



($\text{R}^1 = \text{R}^2 = \text{H}$) was detected by GC/MS analysis of the vapor phase of the decomposed reaction mixture at -20°C ($M^+ = 42$). Although we could not carry out quantitative analysis of **11a**, a small amount of ketene **11a** was detected by GLC analysis. The elimination of the ketene [6] was found to be reversible by the following experiment. The ferrocenolate **2a** prepared at -78°C was warmed up to

TABLE 2
REACTIONS OF FERRAENOLATE **1a** WITH ALKYL HALIDES

$$\text{CpFe}(\text{CO})_2\text{COCH}_3 \xrightarrow[\text{(2) R-X, } -78^\circ\text{C} \rightarrow -20^\circ\text{C}]{\text{(1) LiN}(\text{SiMe}_3)_2, -78^\circ\text{C}, 1\text{h}} \text{CpFe}(\text{CO})_2\text{COCH}_2\text{-R} + \text{CpFe}(\text{CO})_2\text{-R}$$

(1a) (7) (8)

R-X	Products (Yield, %) ^a
Me-I	7 (99)
Et-I	8 (32)+ 9 (48) ^b
Pr ⁱ -I	8 (28)+ 9 (42) ^b
Me ₃ SiCH ₂ -I	8 (54)
PhCH ₂ -Br	8 (54)

^a Yields were determined by ¹H NMR using benzene as an internal standard. ^b **9** = [CpFe(CO)₂]₂.

-20°C for 30 min and then half the reaction mixture (I) was treated with MeI. The remaining half was recooled to -78°C for 30 min (II) and successively treated with MeI. The product distributions after purification by column chromatography are summarized in Table 3. The following resulted: (1) the ferraenolate **2a** dissociates into the ferrate **10** and ketene **11a** at -20°C and (2) they recombine with each other to reproduce the ferraenolate **2a** upon recooling. Thus, eq. 3 turns out to be reversible and the equilibrium is shifted to the right at higher temperature.

Meanwhile, the phosphine-substituted derivative, Li[CpFe(CO)(PPh₃)(COCH₂)] (**12**) [1a-d], was found to be stable even at room temperature. The ease of ketene elimination might be governed by the thermodynamic stability or the basicity of the liberated ferrate anion ([CpFe(CO)₂]⁻ vs. [CpFe(CO)(PPh₃)]⁻). The dicarbonyl ferrate **10** is far more stabilized by the electron-withdrawing effect of the carbonyl ligand through π back-donation. In addition, we found that the corresponding molybdenum systems, CpMo(CO)₂(PR₃)(COCH₃) (PR₃ = PPh₃, PPhMe₂, PBu₃,

TABLE 3
REVERSIBLE ELIMINATION OF KETENE FRAGMENT FROM FERRAENOLATE **1a**

$$\text{CpFe}(\text{CO})_2\overset{\text{O}}{\parallel}\text{CCH}_3 \xrightarrow[\text{-78}^\circ\text{C} / 30\text{ min}]{\text{LiN}(\text{SiMe}_3)_2} \text{Li}[\text{CpFe}(\text{CO})_2\overset{\ominus}{\text{C}}\text{CH}_2] \xrightarrow[\text{30 min}]{-20^\circ\text{C}} \text{(I)} \xrightarrow[\text{30 min}]{-78^\circ\text{C}} \text{(II)}$$

Me-I

Products ^a (Yields, %) ^b	Fp-COCH ₂ -Me <u>3a</u>	Fp-Me <u>4a</u>	Fp-COCH ₃ <u>1a</u>	Fp-Fp <u>9</u>
(I) + Me-I	18	60	7	5
(II) + Me-I	68	5	10	5

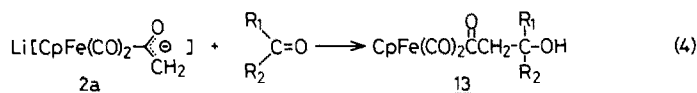
^a: Fp = CpFe(CO)₂.

^b: Yields were determined by ¹H-NMR using benzene as an internal standard.

P(OPh)₃, P(OBu)₃), spontaneously eliminated ketene upon treatment with LDA at -78°C, since the molybdate was known to be far more stable (less basic) than the ferrate [7].

Even slightly hindered substrates such as EtI did not directly react with **2a** at -78°C but reacted with **10** after ketene elimination during warming up to room temperature to give alkyl complexes **8**. The inertness of **2a** toward hindered alkyl halides at low temperature was verified by the following experiment. Treatment of **2a** with EtI at -78°C for 30 min and subsequent addition of MeI to the mixture resulted in the exclusive formation of the enolate adduct **3a**. Similar behavior was observed for the ferraenolate **2b** derived from the propionyl complex **1b**. The relative reactivity of the anionic species **2** to **10** was also an important factor, since **10** should be preferentially trapped by an alkyl halide due to its higher nucleophilicity. However, it was recently reported by Helquist et al. that highly electrophilic alkyl trifluoromethanesulfonates reacted with the ferraenolate **2a** to give the enolate adducts [1e].

Carbonyl compounds readily reacted with the ferraenolate **2a** giving the expected aldol adducts **13** (eq. 4). Ketene elimination was not observed at all even in the



a: R₁=R₂=Me (34%)

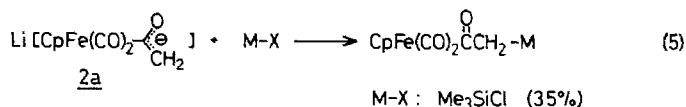
b: R₁=R₂=(CH₂)₅- (70%)

c: R₁=R₂=Ph (54%)

d: R₁=H, R₂=Ph (67%)

reaction with hindered substrates such as benzophenone. However, hindered substrates bearing an acidic proton such as 3,3-dimethyl-2-butanone and 2,4-dimethyl-3-pentanone were merely deprotonated by the enolate **2a** to regenerate the starting acetyl complex **1a**.

Finally, we attempted the preparation of μ -ketene complexes by the reaction of ferraenolate **2a** and **12** with metal halides (CpFe(CO)₂Cl, CpMo(CO)₃I, Me₃SiCl etc.). Only Me₃SiCl gave the adduct (eq. 5) and others gave dimetallic complexes



free from ketene fragments.

Experimental

All manipulations were carried out by the standard Schlenk tube technique under argon. THF was dried over Na/K alloy, distilled and stored under argon. Other organic reagents were used as purchased without further purification. Column chromatography was performed on alumina (activity II-III) unless otherwise noted.

¹H NMR spectra were recorded on a Hitachi High Resolution NMR Spectrometer R24B (60 MHz) and a JEOL FX-100 (100 MHz) using CDCl₃ as a solvent. IR spectra were obtained on a Hitachi 260-50 apparatus. Mass spectra were recorded on

a Hitachi Gas Chromatograph-Mass Spectrometer M-80 using a column packed with Porapak Q and elemental analyses were carried out using the analytical facility in the Research Laboratory of Resources Utilization at the Tokyo Institute of Technology. Melting points were measured with a Buchi Melting Point Determinator 510 in a sealed tube and were uncorrected.

The acyl complexes **1** [8], $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$ [9] and $\text{CpMo}(\text{CO})_2(\text{PR}_3)_2(\text{COCH}_3)$ [10] were prepared by the reported methods.

Generation of ferraenolate and the reaction with alkyl halides

Lithium bis(trimethylsilyl)amide (prepared from *n*-butyllithium (2.3 mmol, 1.6 M in hexane, 1.4 ml) and hexamethyldisilazane (2.3 mmol, 0.33 ml) in 3 ml THF at 0°C) was added to the acetyl complex **1a** (1.9 mmol, 415 mg) dissolved in 5 ml THF at -78°C. After stirring for 40 min MeI (1.9 mmol, 0.12 ml) was added dropwise to the resulting ferraenolate and the mixture was further stirred at -78°C for 60 min and at room temperature for 60 min. The solvent was then removed under reduced pressure and the residue was chromatographed on alumina (2 cm \times 10 cm, pentane eluent) to give the propionyl complex **3a** (396 mg, 1.7 mmol, 90% yield) as an orange red oil. The structure was confirmed by comparison of the spectral data (¹H NMR, IR) with those of an authentic sample [8b] and by elemental analysis. Found: C, 51.68; H, 4.43. $\text{C}_{10}\text{H}_{10}\text{O}_3\text{Fe}$ calcd.: C, 51.32; H, 4.31%.

The reactions with other alkyl halides were carried out similarly and the structure of the resulting alkyl complexes was identified by comparison of the spectral data with those of the authentic samples [11].

The reaction of acyliron complexes 1 with LDA

The acyliron complex **1** was treated similarly with LDA in place of $\text{LiN}(\text{SiMe}_3)_2$. **1a** and **1b** gave mixtures of products, **3a** (68%) + **4a** (27%) and **4b** (80%) + **4c** (16%), respectively. They could not be separated from each other by the usual chromatographic purification so that the structure was determined by ¹H NMR. **1c** gave **4c** in 95% yield.

4a [12]: ¹H NMR δ 5.38 (2H, t, J 2.2 Hz, Cp), 4.92 (2H, t, J 2.2 Hz, Cp), 2.45 (3H, s, COCH_3), 0.24 (3H, s, Me) ppm. **4b**: ¹H NMR δ 5.35 (2H, t, J 2.2 Hz, Cp), 4.90 (2H, t, J 2.2 Hz, Cp), 2.69 (2H, q, J 7.3 Hz, COCH_3), 1.19 (3H, t, J 7.3 Hz, COCH_2CH_3), 0.25 (3H, s, Me) ppm. **4c**: deep red oil. Found: C, 55.39; H, 5.62. $\text{C}_{12}\text{H}_{14}\text{O}_3\text{Fe}$ calcd.: C, 54.99; H, 5.38%. ¹H NMR δ 5.34 (2H, t, J 2.2 Hz, Cp), 4.92 (2H, t, J 2.2 Hz, Cp), 2.94 (1H, sept, J 6.6 Hz, COCH), 1.19 (6H, d, J 6.6 Hz, $\text{CH}(\text{CH}_3)_2$), 0.25 (3H, s, Me) ppm. IR (neat) 2004, 1953 $\nu(\text{C}\equiv\text{O})$, 1674 $\nu(\text{C}=\text{O})$ cm^{-1} .

Reversible ketene elimination

The acetyl complex **1a** (535.9 mg, 2.44 mmol) was treated with 2.92 mmol of $\text{LiN}(\text{SiMe}_3)_2$ in 10 ml THF at -78°C and the mixture was stirred at -78°C for 30 min and subsequently at -20°C ($\text{CCl}_4/\text{solid CO}_2$ bath) for 30 min. The resulting reaction mixture was divided into two portions with a syringe. One portion was treated with MeI (2.0 mmol, 0.124 ml) at -20°C. The other portion was recooled to -78°C for 30 min with stirring and then treated with MeI (2.0 mmol, 0.124 ml).

The obtained reaction mixtures were evaporated under reduced pressure and the residue was chromatographed on alumina (eluted with dichloromethane). The colored band was collected and the solvent was removed in vacuo.

The products were identified by comparison of ^1H NMR spectra with those of the authentic samples and the yields were calibrated using benzene as internal standard.

Attempted generation of metallaenolate from acetylmolybdenum complexes

The acetylmolybdenum complexes, $\text{CpMo}(\text{CO})_2(\text{PR}_3)(\text{COCH}_3)$, were treated with 1.2 equivalent of LDA at -78°C in THF. After 5 min MeI (1.2 equivalent) was added dropwise and the mixture was gradually warmed to room temperature during 30 min. The resulting mixture was worked up as described above. Separation by column chromatography gave $\text{CpMo}(\text{CO})_2(\text{PR}_3)\text{Me}$ (50–80% yield), $\text{CpMo}(\text{CO})_3\text{CH}_3$ and unreacted $\text{CpMo}(\text{CO})_2(\text{PR}_3)\text{COCH}_3$. $\text{CpMo}(\text{CO})_3\text{CH}_3$ might be produced from the acetyl complex by removal of the phosphine ligand by MeI as $(\text{MePR}_3)\text{I}$ and subsequent methyl migration to the coordinatively unsaturated metal center. This process was verified by the direct reaction of the acetyl complex with MeI. In addition, $\text{LiN}(\text{SiMe}_3)_2$ could not abstract any proton from the acetyl complexes.

Reactions of ferraenolate 2a with carbonyl compounds

The ferraenolate **2a** was treated with carbonyl compounds (1.5 equivalent) in a similar manner to the reaction with MeI. The products were purified by column chromatography (alumina) using ethyl acetate as an eluent. The spectral data of the products shown in Table 4 were consistent with the β -hydroxyacyl complex.

TABLE 4
SPECTRAL DATA OF β -HYDROXYACYLIRON COMPLEXES 13

Compound	^1H NMR δ (ppm) in CDCl_3 (100 MHz)	IR (cm^{-1}) KBr pellet	Analysis (Found (calcd.) (%))	Melting point ($^\circ\text{C}$)
13a	1.16 (6H, s, CH_3)	3453 $\nu(\text{OH})$	C: 50.65 (51.83) H: 4.92 (5.07)	68.0–69.0
	3.11 (2H, s, CH_2)	2019 $\nu(\text{C}\equiv\text{O})$		
	3.81 (1H, s, OH)	1960 $\nu(\text{C}\equiv\text{O})$		
	4.87 (5H, s, C_5H_5)	1622 $\nu(\text{C}=\text{O})$		
13b	1.09–1.77 (10H, m, $(\text{CH}_2)_5$)	3445 $\nu(\text{OH})$	C: 56.43 (56.63) H: 5.69 (5.70)	76.0–77.0
	3.09 (2H, s, CH_2)	2008 $\nu(\text{C}\equiv\text{O})$		
	3.65 (1H, s, OH)	1962 $\nu(\text{C}\equiv\text{O})$		
	4.86 (5H, s, C_5H_5)	1607 $\nu(\text{C}=\text{O})$		
13c	3.27 (2H, d, J 8.0 Hz, CH_2)	3445 $\nu(\text{OH})$	C: 58.43 (58.93) H: 4.27 (4.33)	84.0–85.0
	3.36 (1H, d, J 4.0 Hz, OH)	2034 $\nu(\text{C}\equiv\text{O})$		
	4.83 (5H, s, C_5H_5)	1950 $\nu(\text{C}\equiv\text{O})$		
	5.03 (1H, dt, J 4.0 and 8.0 Hz, CH)	1620 $\nu(\text{C}=\text{O})$		
	7.32 (5H, brs, Ph)			
13d	3.91 (2H, s, CH_2)	3370 $\nu(\text{OH})$	C: 64.27 (64.69) H: 4.50 (4.51)	131.0–132.0
	4.73 (5H, s, C_5H_5)	2014 $\nu(\text{C}\equiv\text{O})$		
	5.05 (1H, s, OH)	1955 $\nu(\text{C}\equiv\text{O})$		
	7.13–7.45 (10H, m, Ph)	1599 $\nu(\text{C}=\text{O})$		

Reaction of ferraenolate 2a with Me₃SiCl

The ferraenolate **2a** was similarly treated with Me₃SiCl at -78°C . Purification by column chromatography (Florisil, pentane elution) gave CpFe(CO)₂COCH₂SiMe₃ (35% yield) as a yellow oil. ¹H NMR δ 4.84 (5H, s, Cp), 2.83 (2H, CH₂), 0.11 (9H, s, SiMe₃) ppm. IR (neat) 2004, 1959 $\nu(\text{C}\equiv\text{O})$, 1626 $\nu(\text{C}=\text{O})$, 1249 $\nu(\text{Si}-\text{C})$ cm⁻¹.

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